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Preparation and characterization of methylic and ethylic biodiesel from cottonseed oil and effect of tert-butylhydroquinone on its oxidative stability

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ABSTRACT

This work reports the preparation and characterization of methylic and ethylic biodiesel from cottonseed oil. Biodiesel was prepared by a transesterification process involving the reaction of the oil with methanol or ethanol using KOH as catalyst. The conversion of triglycerides to the corresponding methyl and ethyl ester was 91.5 and 88.5 (wt%). All the physical–chemical properties of the obtained biodiesels met the minimum or maximum limits of the EN 14214 except oxidation stability. The addition of the synthetic antioxidant tert-butylhydroquinone at the concentration of 300 mg kg^{-1} was sufficient to obtain acceptable oxidation stability values (>6 h). Thermogravimetric analysis was also performed and similar profiles were verified for both ethylic and methylic biodiesels. Therefore, this work demonstrates the feasibility of using the ethanolic route to produce cottonseed oil biodiesel.

1. Introduction

Research on renewable energy sources has become crucial due to the diminishing reserves of oil and increased pollution from the burning of fossil fuels. As a proposal for an alternative renewable fuel, biodiesel produced from different vegetable oils, waste cooking oil and animal fat has received great attention in industry and academia. Biodiesel is a promising substitute for petroleum-based fuels, especially for diesel oil, due to its similar physical properties, and therefore, does not require adaptations of diesel engines and storage infrastructure [1].

The oil from several seeds such as soybeans, canola, corn, sunflower, jatropha, coconut, palm and castor oil was used for the production of biodiesel, mainly by the transesterification reaction with short chain alcohols (methanol or ethanol) employing alkaline catalysts [2]. Much of this oil can be produced in Brazil due to favorable soil and climatic conditions, in addition to its extensive territorial [3].

The cottonseed oil is the oldest vegetable oil used industrially produced and widely consumed in Brazil. Consumption decreased with the increase in soybean production, but still occupies a place of great economic importance. The cottonseed contains 14–25% in average oil, and 1.2% of myristic acid, 18–25% of palmitic acid, 1–25% of stearic acid, 1–2% of palmitoleic acid, 17–38% of oleic acid and 45–55% of linoleic acid [4].

Biodiesel from cottonseed oil was evaluated in diesel engines, and it was found that reducing the emission of carbon monoxide, particulate matter, sulfur dioxide and smoke, however, the emission of nitrogen oxides slightly increased [5,6]. Blends of methyl cottonseed oil biodiesel and diesel were evaluated using diesel engines and it was also verified reduction of particulate matter emission by 46.6% [7]. Additionally, it was found that the alternative fuel had a high calorific value and cetane number, as well as low sulfur and aromatics, without compromising the engine performance [7]. The storage at low temperature of blends of cottonseed biodiesel and diesel has been investigated and the formation of precipitates was predominant in blends with higher amounts of biodiesel [8]. However, the use of anti-gel additives improved the low temperature operability of cottonseed biodiesel [9].

The conventional and in situ transesterification of cottonseed oil with methanol and ethanol in the presence of NaOH was evaluated exploring mechanical stirring and ultrasonication [10]. The authors verified that in situ and conventional transesterification gave similar yields of methyl esters and that the use of ultrasonication for the methylic route provided lower yields than using mechanical stirring [10]. Microwave irradiation was found to reduce substantially the reaction time of alkali-catalyzed transesterification of cottonseed oil from 30 min using conventional heating to 7 min [11]. Demirbas described the production of biodiesel through the transesterification process of cottonseed oil using non-catalytic supercritical methanol and ethanol [12].

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Alternatively, the high-speed enzymatic production of cottonseed oil biodiesel by methanolysis in a continuous reactor was described [13,14]. Recently, the biodiesel production from cottonseed oil through conventional alkaline transesterification using methanol and NaOH as catalyst was evaluated [15]. The highest yield percentage was obtained using 6:1 (v/v) methanol–oil ratio and 1% (wt.) NaOH at 60 °C for 1 h [15]. The physical–chemical properties of the obtained biodiesel were compared with specification norm for diesel oil except oxidation stability which was not performed [15]. Previous study exploiting different catalysts (NaOH, KOH, sodium methoxide, and potassium methoxide) was performed [16]. The highest yield was obtained using 6:1 (v/v) methanol–oil ratio and 0.75% (wt.) sodium methoxide at 65 °C for 90 min [16].

This work describes the preparation and characterization of biodiesels obtained through conventional alkaline transesterification of cottonseed oil by methylic and ethylic routes. The oxidation stability of the obtained biodiesel was improved by the addition of the antioxidant tert-butylhydroquinone (TBHQ).

2. Experimental

2.1. Reagents and samples

The refined cottonseed oil was donated from Cargil® (Uberlândia, Brazil). Tert-butylhydroquinone (TBHQ) (97% m/m) was purchased from Acros Organics (New Jersey, USA). Analytical-grade ethanol, methanol, and potassium hydroxide were purchased from Synth (São Paulo, Brazil). Free fatty acids in the samples were determined using internal stock solution (methyl heptadecanoate and *n*-heptane) from Sigma–Aldrich (São Paulo, Brazil).

2.2. Synthesis of biodiesel and its physical–chemistry properties

Biodiesel from cottonseed oil was produced by transesterification of the oil with methanol and ethanol under reflux conditions. Methanol (5:1 molar ratio, alcohol/oil) with 99.8% of purities or ethanol (6:1 molar ratio, alcohol/oil) with 99.99% of purities was added to the reactor followed by the slow addition of a catalyst (1% w/w KOH/oil) with 90% of purities under stirring until the complete dissolution of the catalyst at 25 °C. The time reaction for the methylic and ethylic routes was 1 and 2 h, respectively. After the end of reaction, the glycerine phase was removed and the biodiesel was washed with hot water (~85 °C) until obtaining a final pH around 7. The biodiesel was washed with four portions of 50 mL of hot water. The biodiesel was kept inside amber glass flasks until analysis, after a water-removal step by evaporation using a rotary evaporator for 1 h at 85 rpm and 80 °C. The acid index, viscosity, oxidation stability, gas chromatography, thermogravimetric analysis, flash point and peroxide index were measured. The standards test methods are identified showed in Table 2. The acid and peroxide indexes were measured in an automatic titrator Titrino plus 848 (Metrohm). The viscosity was measured in a bath automatic viscometer (ISL PAC Instruments). The flash point was determined in a Cleveland open vessel using nearly 75 mL of sample.

Table 1
Fatty acid methyl ester composition of the methylic (MB) and ethylic (EB) biodiesels ($n = 3$).

Fatty acid methyl ester	CN/DB abbreviation[a]	MB (wt%)	EB (wt%)
Myristic	C14:0	0.70 ± 0.05	0.70 ± 0.05
Palmitic	C16:0	22.8 ± 0.1	23.2 ± 0.01
Stearic	C18:0	2.40 ± 0.06	2.40 ± 0.05
Oleic	C18:1	15.5 ± 0.1	15.8 ± 0.1
Linoleic	C18:2	57.6 ± 0.2	55.6 ± 0.1
Linolenic	C18:3	0.30 ± 0.05	0.30 ± 0.05
Others	–	0.7	2.0
Saturated	–	25.9	26.3
Unsaturated	–	74.1	73.7

[a] CN = carbon number; DB = number of double bonds.

2.3. Gas chromatography analysis

The fatty ester composition of biodiesel was determined by a gas chromatograph model 7890A (GC, Agilent Technologies, USA) with a CPWAX 52CB capillary column (30 m × 0.25 mm × 0.15 μm), 0.5 μL as injection volume (injector at 250 °C), oven at 170 °C, flame ionization detector (FID) at 390 °C with a hydrogen pressure of 200 kPa and flow rate of 2 mL min^{-1}. The analysis was carried out in triplicate. The analysis of fatty esters was performed following the EN14103:2003 method in which methyl heptadecanoate was used as an internal standard. Sample and standard were diluted in *n*-heptane. The identities of the fatty esters were determined based on the retention time of methyl heptadecanoate. The composition of fatty esters was calculated according to the area of the peaks. The result for the fatty acid methyl ester content is expressed as a mass fraction in percent using methyl heptadecanoate.

2.4. Oxidation stability

Oxidation stability measurements were carried out using Rancimat equipment model 873 (Metrohm, Herisau, Switzerland) in accordance with EN 14112. In this method, the oxidation of biodiesel was induced by passing air at a flow rate of 10 L/h through the sample (3 g) and then through a water trap (deionised water). At the same time, the sample flask was kept at 110 °C. All samples were tested in triplicate.

2.5. Thermogravimetric analysis (TGA)

TGA curves were obtained in a DTG-60 Shimadzu thermobalance, using aluminum pans. The experiments were carried out under continuous nitrogen flow of 70 mL min^{-1}, and the temperature ramp was set at 10 °C min^{-1}. The weight loss was recorded from 10 to 600 °C.

3. Results and discussion

The refined cottonseed oil used for biodiesel production showed acid value of 0.52 mg KOH g^{-1} oil, saponification index of 170 mg KOH g^{-1} oil, kinematic viscosity (40 °C) of 44.16 mm^2 s^{-1}, 19.03 h of induction time (oxidation stability) and 470 mg Kg^{-1} of water. These values are within acceptable limits for refined oils and thus this oil was considered suitable for the production of biodiesel. The acid value (limit of 6 mg KOH g^{-1} oil) results in the formation of soap when using alkaline catalysts, which leads to lower yields of esters [10]. The reason for yield loss is the dissolution of esters in the glycerol phase by K or Na salts of FFAs, originated either from hydrolysis or from the raw material [17,18]. Additionally, previous work has reported that oils with 2 mg KOH g^{-1} or lower produces maximum yield by homogeneous base catalyzed transesterification [19]. Based on the acid value obtained, the alkaline transesterification was selected to produce methylic and ethylic biodiesels.

The saponification index of the cottonseed oil was lower than of other vegetable oils reported in the literature, which indicated low concentration of low molecular weight triglycerides [20]. The higher the index, the greater the amount of base required for the reaction to occur, so that value justifies the use of only 1% m/m as

Table 2
Physical–chemical properties of the methylic (MB) and ethylic (EB) biodiesels.

Property (units)	Mean (MB)	Mean (EB)	EN 14214 limits	EN 14214 method
Flash point (°C)	170 ± 2	168 ± 2	Min. 120	EN ISO 3679
Viscosity (mm^2/s, at 40 °C)	4.45 ± 0	4.51 ± 0	3.5–5.0	EN ISO 3104
Density (g/cm^3, at 20 °C)	0.882 ± 0.001	0.887 ± 0.001	0.860–0.900	EN ISO 3675
Acid value (mg of KOH/g)	0.17 ± 0.02	0.16 ± 0.01	Max. 0.5	EN 14104
Free glycerol (% w/w)	0.008 ± 0.001	0.009 ± 0.001	Max. 0.01	EN 14105, EN 14106
Total glycerol (% w/w)	0.21 ± 0.01	0.18 ± 0.02	Max. 0.38	EN 14105, EN 14106
Oxidation stability (h, at 110 °C)	4.9 ± 0.8	4.8 ± 0.6	Min. 6	EN 14112
Peroxide value (meq/kg)	11 ± 0.3	12.9 ± 0.4	–	[a]
Moisture (ppm)	248 ± 1	372 ± 2	500	EN ISO 12937

[a] American Oil Chemists' Society – official method Cd8-53.

catalyst for the oil, unlike most of the routes that use 2–3% of alkaline catalyst [5–11,21].

Table 1 presents the fatty ester composition of the cottonseed oil biodiesel obtained by methylic and ethylic routes. Table 2 lists the physical–chemical properties of the obtained biodiesels. The yields of esters produced by methylic and ethylic routes were 91.5% and 88.5%, respectively. The biodiesel mainly consisted of unsaturated fatty acid esters (>70 wt%), which mainly included linoleic (C18:2), palmitic (C16:0), and oleic (C18:1) (in Table 1). This result is not in complete agreement with previous reports for biodiesel produced from cottonseed oils from the Mediterranean region [10,11]. Lower amount of palmitic acid and higher amount of stearic acid were found in the oil used in this work in comparison with the cottonseed oil from the Mediterranean region (26–29% of palmitic acid and 0.9–1.3% of stearic acid). Moreover, myristic acid was not found in the composition of cottonseed oils of previous works [10,11].

The physical–chemical properties of biodiesels met the minimum or maximum limits of the EN 14214 except the values of oxidation stability. The kinematic viscosity values indicated the high-efficient conversion of triglycerides into esters. The flash point values are related to the flammability of fuel and may indicate the presence of residual alcohol in biodiesel, which would reduce this value.

The acid, peroxide and moisture contents and composition of fatty acid esters (unsaturated) are related to the oxidative stability of biodiesel. The acid values for both biodiesels were similar and considered acceptable. The moisture content was higher in the ethylic biodiesel, but both biodiesels met acceptable levels. Fuels with high acid content present corrosive character which is a considerable drawback during storage and transport of biodiesel. Biodiesel oxidation processes are accelerated in the presence of water and oxygen, and in the presence of pro-oxidants agents [21,22]. As a consequence of these oxidative processes, there is an increase in peroxide content of biodiesel, which is proportional to the oxidative instability of biodiesel, that can lead to changes in the physical–chemical properties of biodiesel such as increased viscosity and density, besides the formation of gums and sediments that impair the functioning of motor [21,22]. The predominance of linoleic acid (C18:2) in the cottonseed oil biodiesel may contribute to the low values of induction time (4.9 h which was below the minimum established by EN 14214), since the instability to oxidation of biodiesel is proportional to the number of unsaturated fatty acids. A previous work which reported the production of biodiesel from cottonseed oil and measured the oxidation stability found 1.9 h as induction time [16], which was much lower than the value obtained in this work. The oxidation mechanism of biodiesel compounds has been investigated [23,24], and the primary oxidation products of double or triple bonds are allylic hydroperoxides. Thus the greater the number of unsaturations in the fatty acids, lower oxidation stability is verified.

To increase the oxidative stability of biodiesel and slow oxidative degradation processes, synthetic antioxidants may be added into biodiesel [25–29]. In this study, TBHQ was selected because of its proven efficacy compared to other synthethic antioxidants [25–28]. Fig. 1 shows the change in oxidative stability (induction time) of methylic biodiesel after additions of increasing concentrations of TBHQ.

According to Fig. 1, from the addition of 300 mg kg^{-1}, biodiesel from cottonseed oil methyl met the threshold established by 6 h ANP. In the same figure it appears that the oxidative stability of biodiesel increases linearly with the concentration of antioxidant.

The thermogravimetric analysis was realized for cottonseed oil and for methylic and ethylic biodiesels. The Fig. 2 presents the thermogravimetric curves for the cottonseed oil and for the respective methylic and ethylic biodiesels obtained by transesterification.

As expected, the thermal stability of cottonseed oil is higher than of obtained biodiesels. The pyrolysis in all cases occurs at a single step. The thermal degradation of the cottonseed oil started at around 290 °C and of both biodiesels at around 135 °C. The higher thermal stability of the oil is related to its structure typically composed of tryacylglycerol (higher molecular weight) whilst the biodiesel is composed by a mixture of free esters. Moreover, the presence of antioxidants in the oil (200 mg kg^{-1}) may have contributed to the higher thermal stability. The pyrolytic process of biodiesel involved the decomposition reaction of the free esters possibly resulting in the formation of alkyls, carboxylates and water [30,31]. The thermogravimetric profiles for both methylic and ethylic biodiesels are similar and in agreement with oxidation stability parameter values which were very similar for both biodiesels.

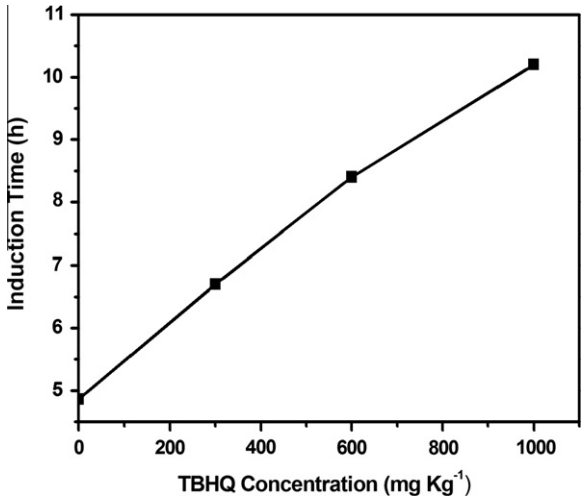

Fig. 1. Behavior of induction time of the methylic biodiesel upon increasing additions of TBHQ.

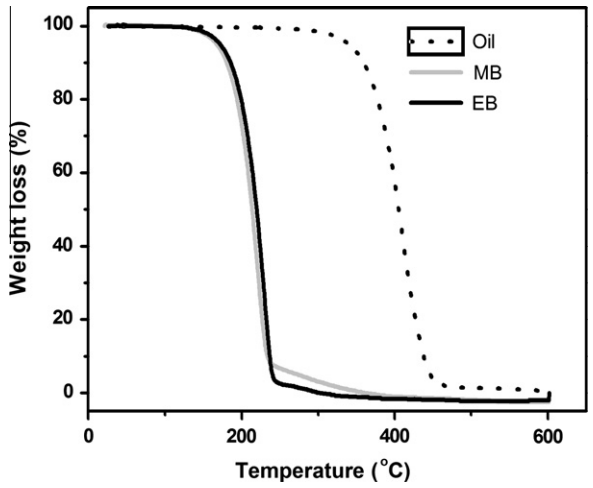

Fig. 2. Thermogravimetric curves obtained for the cottonseed oil (oil), methylic biodiesel (MB) and ethylic biodiesel (EB).

4. Conclusion

The production of biodiesel from cottonseed oil through methylic and ethylic routes showed satisfactory performance for both cases. The physical–chemical characteristics of both biodiesels were closely similar and met the limits established by EN 14214, with the exception of oxidative stability. To overcome such a drawback, the addition of 300 mg kg^{-1} TBHQ was sufficient to attend the oxidation stability parameter. Thus, the ethylic route can be employed for biodiesel production from cottonseed oils within acceptable limits for commercialization of the biofuel. Additional advantage is related to the use of bioethanol for biodiesel production, which is a less toxic and renewable source and has its production fully consolidated in Brazil.

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